Supporting Information for

Role of Ligand Protonation in Dihydrogen Evolution from a Pentamethylcyclopentadienyl Rhodium Catalyst

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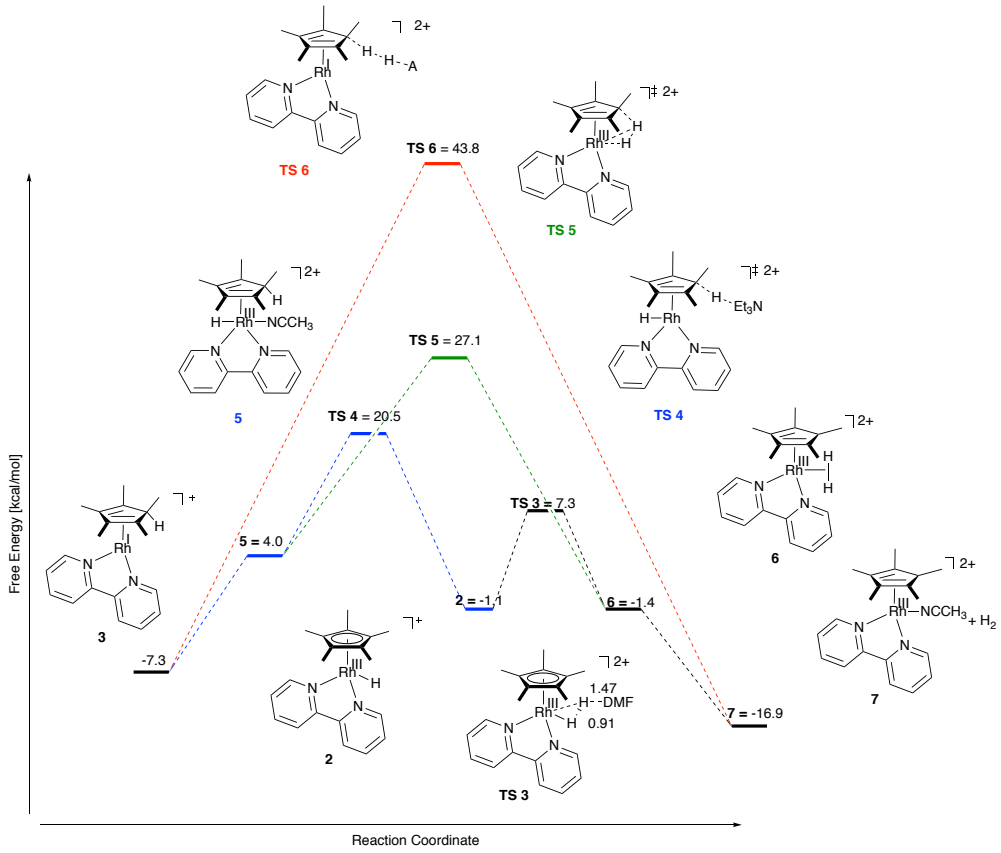
Appendix 1: Scheme S1: Additional protonation transition states



Scheme S1: Additional protonation states **TS 5** and **6** are shown.

Both direct attack by the acid at the protonated Cp* ring (**TS 6**) and the metathesis pathway (**TS 5**) feature barriers that are thermally inaccessible at room temperature. In the case of **TS 6**, protonation would lead directly to the evolution of hydrogen, represented by **7**, without the participation of the Rh center. However, at 43.8 kcal/mol above the singly-protonated Rh^{I} complex, this is an insurmountable barrier. Alternatively, after the barrierless generation of **5**, metathesis could occur wherein the metal-bound proton and the Cp*-bound proton combine to generate complex **6**. The barrier for this reaction is found to be 27.1 kcal/mol. By comparison, **TS 4**, which is featured in the manuscript, is 20.5 kcal/mol. Neither of these transition states are reasonable when compared to the concerted pathways.

Appendix 2: Molecular Geometries

Molecular geometries are contained in an additional supplemental file and are in the XYZ format. The titles of the individual complexes correspond with complex names used in this manuscript. They can be viewed using several free programs available online including Mercury (www.ccdc.cam.ac.uk/mercury).

Appendix 3: Calculation Details

Table S1. Components of free energies for all unsubstituted molecules along the pathway (in kcal/mol unless otherwise specified)

Molecule	ZPE	Hvib	Svib	6kT	1/2 (Strans+Srot) + Selec	Selec	Htot	Stot	G(solv) [Hartree]	E(SCF) [Hartree]	G (total)
7	271.175	15.116	102.661	3.553	39.548	0.000	17.486	176.280	-0.20755	-1126.83365	-706982.7
1	239.494	12.184	79.478	3.553	39.140	0.000	14.554	152.270	-0.00357	-994.59532	-623901.5
3	248.555	12.674	79.408	3.553	39.187	0.000	15.044	158.720	-0.05462	-995.02012	-624190.5
3X	248.418	12.664	79.186	3.553	39.156	0.000	15.034	158.510	-0.05500	-995.01916	-624190.2
2	246.435	12.730	79.248	3.553	39.135	0.000	15.100	158.220	-0.05666	-995.00506	-624184.4
TS 1a	376.896	19.088	121.859	3.553	40.208	0.000	21.458	204.500	-0.05139	-1287.25831	-807449.0
TS 1b	377.273	19.001	120.540	3.553	40.384	0.000	21.371	202.470	-0.05122	-1287.26603	-807453.1
TS 1c	376.360	19.180	123.272	3.553	40.152	0.000	21.550	204.450	-0.05097	-1287.28394	-807465.7
TS 2	244.914	12.541	77.739	3.553	39.168	0.000	14.911	156.570	-0.05438	-994.97941	-624168.1
6	250.655	12.905	83.564	3.553	39.116	0.000	15.275	156.310	-0.21959	-995.26462	-624446.4
5	284.252	15.964	105.148	3.553	39.636	0.000	18.334	185.070	-0.20638	-1127.99198	-707695.7
TS 4	318.273	17.361	114.003	3.553	40.058	0.000	19.731	196.430	-0.19977	-1243.70425	-780269.5
TS 6	346.356	20.692	140.626	3.553	40.512	0.000	23.062	225.390	-0.18950	-1376.38954	-863501.0
TS 3	316.096	17.607	116.413	3.553	40.020	0.000	19.977	198.730	-0.19985	-1243.72115	-780282.8
TS 5	251.045	12.557	77.422	3.553	39.135	0.000	14.927	155.950	-0.21917	-995.22251	-624417.8

Table S2. Calculated Free energies in kcal/mol.

Molecule	DeltaG
TS 1a	19.9
TS 1b	15.8
TS 1c	3.2
TS 2	15.2
3	-7.3
2	-1.1
3X	-7.0
	-4.0
6	-1.4
5	4.0
TS 4	20.6

TS 6	43.8
TS 3	7.3
TS 5	27.1

Table S3. Free energy components for substituted complexes (in kcal/mol unless otherwise specified)

Molecule	ZPE	Hvib	Svib	6kT	1/2 (Strans+Srot) + Selec	Selec	Htot	Stot	G(solv) [Hartree]	E(SCF) [Hartree]	G (total)
Methoxy											
Rh1.MeO	280.29	15.56	102.96	3.55	40.11	0.00	17.93	177.97	-0.00825	-1223.58289	-767559.5
Rh1.CpH.MeO	289.60	15.96	101.14	3.55	40.14	0.00	18.33	183.46	-0.05285	-1224.02261	-767853.1
Rh3.H.MeO	287.47	16.03	101.48	3.55	40.09	0.00	18.40	183.23	-0.05500	-1224.00607	-767846.2
NMe2											
Rh1 NMe2	331.08	17.85	119.70	3.55	40.46	0.00	20.22	195.48	-0.00820	-1262.41238	-791877.3
Rh1.CpH.NMe2	340.61	18.32	118.49	3.55	40.49	0.00	20.69	202.25	-0.04792	-1262.86760	-792177.6
Rh3.H.Nme2b	338.52	18.40	118.84	3.55	40.44	0.00	20.77	201.70	-0.05008	-1262.85032	-792170.2
DMPE											
LBdmpe2	271.49	15.22	95.90	3.55	38.83	0.00	17.59	174.87	0.00152	-1420.36858	-891044.9
LBRh1.CpH.dmpe2	279.98	15.23	95.99	3.55	38.86	0.00	17.60	173.81	-0.05405	-1420.78920	-891335.2
LBRh3.H.dmpe2	278.40	15.04	92.87	3.55	38.82	0.00	17.41	171.57	-0.05588	-1420.78746	-891336.1

Table S4. Calculated Free energies of substituted compounds in kcal/mol

group	σ.	ΔG	ΔE(SCF)	Protonation of hydride	Protonation of Cp*
H	0	6.2	9.4	-1.1	-7.3
-CF3	0.54	4.1	8.3	9.9	5.8
-OCH3	-0.27	6.9	10.4	-5.0	-11.9
-NMe2	-0.83	7.4	10.8	-11.1	-18.5
dmpe	1.13	-0.9	1.1		